

## EFFECT OF SEVERITY ON CATALYTIC HYDROPROCESSED SHALE OIL JET FUELS

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### ABSTRACT

Catalytic hydroprocessed shale oil jet fuels in the USA were characterized and compared with petroleum jet fuel to demonstrate their possibility as a conventional jet fuel substitute. The shale oils (Geokinetics, Occidental, Paraho and Tosco II) were hydrotreated in a 0.0508m ID by 11.524m long reactor containing Ni/Mo/Al<sub>2</sub>O<sub>3</sub> catalyst. The fractionated hydrogenated shale oils at jet fuel ranges (120-300°C) were analyzed for composition and physical properties. The increasing hydroprocessing severity proportionally decreased nitrogen, sulfur, olefins, aromatics and increased hydrogen content. The nitrogen content was considerably higher even at high severity conditions. Sulfur and olefin contents were lower at all severities. The heat of combustion and the physical properties, except the freezing point, were comparable to petroleum jet fuels. The yields of jet fuels increased proportionally to increased severity. The study showed that high severity hydroprocessing gave better performance in processing shale oils to jet fuels.

### INTRODUCTION

Shale oil jet fuels contain considerably higher nitrogen levels than petroleum jet fuels. These shale oil-derived jet fuels cannot be processed in a refinery similar to that used to obtain petroleum jet fuel because the high nitrogen content could poison the refinery catalyst. Nitrogen content greater than 5 ppm decreases fuel oil thermal stability and increases nitrogen oxide emissions during jet fuel combustion.

The present problem is to obtain a nitrogen level for jet fuel in the range of 1-5 ppm. High severity hydrodenitritification for the reduction of nitrogen content is not cost effective. The crude jet fuel cut can be chemically treated to lower the nitrogen level to an acceptable upper limit. Hydrogenation of shale oil fractions at low severity, prior to one of the chemical treatments [1] (acid washing, use of an hydrous acid, ion exchange resins, use of solvents, percolation over clays and acid absorbants, partial oxidation) has been shown to substantially lower the cost of producing jet fuel compared to severe catalytic hydrogenation. This hydrogenation operation also reduces the nitrogen level to an acceptable level (1-5 ppm). An increase of temperature [2] and pressure [3] proportionally increase the hydroprocessing severity, which facilitates the removal of nitrogen, sulfur and oxygen and the addition of hydrogen.

In the present work, shale oil hydroprocessing was performed at low, medium and high hydroprocessing severities. The hydroprocessing severity was changed primarily by varying the temperature. Production

Table I Analysis of De-ashed/De-watered and Hydrogenated Shale Oil

Property	PARAFFIN			TOSCO II			CEXIMETICS			OCCIDENTAL						
	D-A/ D-W	T <sub>R</sub> =1.0	T <sub>R</sub> =0.92	T <sub>R</sub> =0.85	D-A/ D-W	T <sub>R</sub> =1.0	T <sub>R</sub> =0.92	T <sub>R</sub> =0.85	D-A/ D-W	T <sub>R</sub> =1.0	T <sub>R</sub> =0.92	T <sub>R</sub> =0.85	D-A/ D-W	T <sub>R</sub> =1.0	T <sub>R</sub> =0.92	T <sub>R</sub> =0.85
Hydrogen Content, Wt. %	11.74	14.00	13.46	12.92	11.23	13.80	13.20	12.34	12.28	13.72	13.31	12.85	12.31	13.60	13.20	12.81
Carbon Content, Wt. %	84.68	85.69	85.42	85.20	84.53	85.43	85.66	85.62	84.45	85.81	85.68	85.61	84.67	86.02	86.13	85.82
Nitrogen Content, Wt. %	2.08	0.19	0.90	1.60	2.15	0.60	0.90	1.61	1.71	0.33	0.74	1.20	1.53	0.25	0.40	1.05
Sulfur (Total), Wt. %	0.71	0.024	0.040	0.051	0.73	0.023	0.042	0.081	0.62	0.01	0.015	0.023	0.67	0.01	0.017	0.043
Density g/ml (60°C)	0.908	0.818	0.840	0.855	0.906	0.837	0.854	0.872	0.876	0.811	0.822	0.840	0.891	0.823	0.841	0.853
Pour Point, °C(°F)	21.2 (81)	23.3 (74)	23.9 (75)	23.3 (74)	20.6 (69)	19.4 (67)	19.4 (67)	21.1 (70)	12.8 (55)	25.0 (77)	23.3 (74)	16.1 (61)	12.2 (54)	23.3 (74)	4.4 (40)	6.1 (41)

of shale oil (Table I) hydroprocessing and distillation of the hydroprocessed product was carried out at NASA's Lewis Research Center bench-scale hydroprocessing facility. The process flow diagram (Figure 1) shows the jet fuel preparation from crude shale oil.

#### EXPERIMENTAL

De-ashed and de-watered shale oil containing 39% hydrocarbons (20% alkanes, 20% aromatics, 25% aromatic resins, 35% olefins and naphthenes) and 61% nonhydrocarbons (60% nitrogen, 10% sulfur and 30% oxygen compounds) was fractionated below 343°C. Shale oil fractions were hydrogenated in a reactor (length 1.524 m and diameter 0.0508m) containing American cyanamide HDS-3A, Ni-Mo/Al<sub>2</sub>O<sub>3</sub> catalyst of .025cm extrusions. The reactor contained four catalyst zones between non-reactive zones of Al<sub>2</sub>O<sub>3</sub> extrusions of 0.3 cm diameter. Alumina zones equipped with wall heat-exchangers maintained nearly constant reaction temperature. The reactor's four catalyst zones were heated by four outside wall electric heaters and the hydrogen preheating (300°C) was accomplished by the electric heater at reactor top. The space velocity of the shale oil liquid in the reactor was 0.99-0.95 m<sup>3</sup>/m<sup>3</sup> hr and the hydrogen consumption was approximately 280 std. m<sup>3</sup>/m<sup>3</sup> of shale oil. Shale oil fractions were hydrotreated at processing severities: (A) high=416°C and 1.413 x 10<sup>4</sup> kpa (B) medium 382°C and 1.396 x 10<sup>4</sup> kpa (C) low = 354°C and 1.327 x 10<sup>4</sup> kpa. Figure 2 demonstrates hydrogen consumption in shale oil at different processing severities. The hydroprocessed shale oil was fractionated (boiling range = 121-300°C) to produce jet fuel. Throughout the discussion, T<sub>R</sub> is a temperature ratio indicating the severity of the run compared with high severity T<sub>R</sub>=1.0-high severity, T<sub>R</sub>=0.92-medium severity, T<sub>R</sub>=0.85-low severity.

#### RESULTS AND DISCUSSIONS

Hydroprocessed shale oil jet fuels were distilled (ASTM 0-86) at different boiling ranges (Figures 3, 4, and 5). The average boiling range of the high, medium and low severity hydroprocessed shale oil jet fuel cuts was 160-190°C for the 10 volume percent distillate and 260-270°C for the 90 volume percent distillate. Low and medium severity jet cuts have higher boiling ranges than high severity cuts because they contain more heavy hydrocarbons and heterocyclic compounds. The distillation temperatures and the volume percent recovery of the shale oil jet fuels are comparable to those of standard petroleum jet fuels (Table II). The results closely agree with the investigations of Shelton [4] who obtained a maximum boiling point of 195°C for 10 volume percent and 255°C for 90 volume percent recovery of a petroleum fuel.

Table II: Petroleum Jet Fuel Properties  
(ASTM Methods)

Hydrogen content, wt%	16.00 max
Aromatics content, vol%	20 max
Nitrogen content (total), ppm	5 max
Sulfur content (mercaptan), wt%	0.003 max
Sulfur content (total), wt%	0.3 max
Naphthalenes content, vol%	3 max
Distillation temperature, °C	-
Initial boiling point	-
10 (vol%)	204 max

Table VII Analysis of Hydroprocessed Shale oil Jet Fuels.

PROPERTY	PARAHO		TOSCO II		GEOKINETICS		OCCIDENTAL	
	T <sub>R</sub> =1.0	T <sub>R</sub> =0.92	T <sub>R</sub> =0.85	T <sub>R</sub> =1.0	T <sub>R</sub> =0.92	T <sub>R</sub> =0.85	T <sub>R</sub> =1.0	T <sub>R</sub> =0.92
Hydrogen Content, wt%	13.85	13.53	13.33	13.78	13.50	13.14	13.68	13.64
Carbon Content, wt%	85.98	85.92	85.33	85.78	85.69	85.46	86.15	85.86
Nitrogen Content, wt%	0.122	0.418	1.16	0.366	0.655	1.16	0.140	0.428
Sulfur Content, wt%	<0.003	0.03	0.032	<0.003	0.022	0.039	<0.003	0.023
Sulfur (Mercaptan), wt%	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003
Aromatics Content, vol. %	19.0	19.7	19.9	22.4	22.5	23.1	19.4	22.0
Olefins Content, vol. %	0.6	3.2	4.5	1.1	1.5	3.3	1.1	1.7
Naphthalenes Content, vol. %	1.12	2.10	3.51	1.76	2.19	3.46	0.96	1.45
Flashpoint, °C (°F)	50.0 (122)	59.4 (139)	59.4 (139)	47.8 (118)	44.4 (112)	43.3 (110)	54.4 (130)	57.2 (135)
Specific Gravity, (15°C/15°C)	0.818	0.830	0.838	0.819	0.829	0.835	0.817	0.831
Freezing Point °C (°F)	-27.8 (-18)	-27.2 (-17)	-27.8 (-18)	-33.3 (-28)	-32.2 (-26)	-30.6 (-23)	-30.8 (-23.5)	-28.9 (-20)
Viscosity, m <sup>2</sup> /s (20°C)	4.2x10 <sup>-6</sup>	4.7x10 <sup>-5</sup>	3.3x10 <sup>-6</sup>	3.5x10 <sup>-6</sup>	0.0x10 <sup>-5</sup>	1.0x10 <sup>-6</sup>	4.0x10 <sup>-6</sup>	4.5x10 <sup>-6</sup>
Heat of Combustion kJ/kg (Btu/lb)	42,282 (18,418)	42,998 (18,485)	42,374 (18,217)	42,549 (18,292)	42,530 (18,284)	42,246 (18,162)	43,072 (18,517)	42,356 (18,209)

50 (vol%)	-
90 (vol%)	-
Final boiling point	300 max
Flashpoint, °C	38 max
Gravity (specific, 15/15°C)	0.7753 to 0.8398
Freezing point, °C	-40
Viscosity at -20°C, m <sup>2</sup> /s	8 x 10 <sup>-6</sup> max
Net heat of combustion, kJ/kg (Btu/lb)	42,800 (18,400) min

Nitrogen content (Figure 6) in all severities is high in Tosco II and low in Occidental jet fuel. The amounts of Weak Base I and non-basic nitrogen compounds are variable in different types of shale oil jet fuels. High severity hydrotreatment significantly decreases [5] the nitrogen content of Weak Base I and non-basic nitrogen compounds, and Weak Base I can be removed more easily than non-basic nitrogen during hydroprocessing. High severity Occidental shale oil contains the lowest amount (0.03 wt%) of nitrogen of all shale oil jet fuels. This amount is significantly higher than that of petroleum jet fuel (1-5 ppm). The nitrogen content in low severity jet fuel is always higher than that of high severity jet fuel.

Table III shows the properties of shale oil jet fuels and also demonstrates that sulfur removal is proportional to severity. High severity jet fuels have the lowest sulfur content (0.003 wt%). Even the sulfur content in low severity jet fuels is lower than that of petroleum jet fuel (0.30 wt% maximum).

Increase of hydrogen content (Table III) in shale oil jet fuels is proportional to the severity of hydrotreatment. Severity increases saturation and cracking of hydrocarbons, thereby increasing the hydrogen/carbon ratio. Gunberger reported [6] the increase of hydrogen content from 11.40 wt% to 13.0 wt%. The hydrogen content (13-14 wt%) in shale oil jet fuel is relatively lower than that of standard petroleum jet fuel, which is 16 wt%. Aromatic content in shale jet fuels decreases with severity because of hydrocracking process. The effect of severity on aromatic content is the highest for Paraho, while Occidental shows the lowest. The aromatic content in shale oil jet fuels (except Paraho) is generally higher than in that of petroleum jet fuel, which is at maximum 20% by volume.

The freezing point of shale jet fuels is significantly higher than that of petroleum jet fuel (-40°F) because shale jet fuels contain higher saturation fractions, particularly higher n-alkanes [7]. Freezing point decreases with increasing severity. Other physical properties such as flash point, viscosity, and specific gravity of the shale jet fuels decrease (Table III) with severity, and the values in all severities are within the acceptable limit of petroleum jet fuel specifications. Severity has little effect on heating values of shale jet fuels and the values are comparable to those of petroleum jet fuels.

#### CONCLUSION

1. High severity shale oil jet fuels constitute the hydrocarbons of more different boiling points than low and medium severity jet fuels. Aromatic and heavy hydrocarbon contents in low and medium severity are higher than in high severity jet fuels.

2. Increasing severity enhances nitrogen and sulfur removal. Nitrogen content is above, while sulfur content is much below, the acceptable limit of that of petroleum jet fuel.
3. Increasing severity increases hydrogen while it decreases aromatic content. Hydrogen content is a little lower while aromatic content is slightly higher than that of petroleum jet fuel.
4. Flash point, viscosity, and specific gravity decrease with increasing severity, and the levels in all severities are within acceptable limits. The freezing point is enhanced with increasing severity and is above the acceptable limit.
5. Increasing severity enhances yields of jet fuels. It can be concluded that high severity hydroprocessed Paraho jet fuel after processing can be considered as an alternative to conventional jet fuel.

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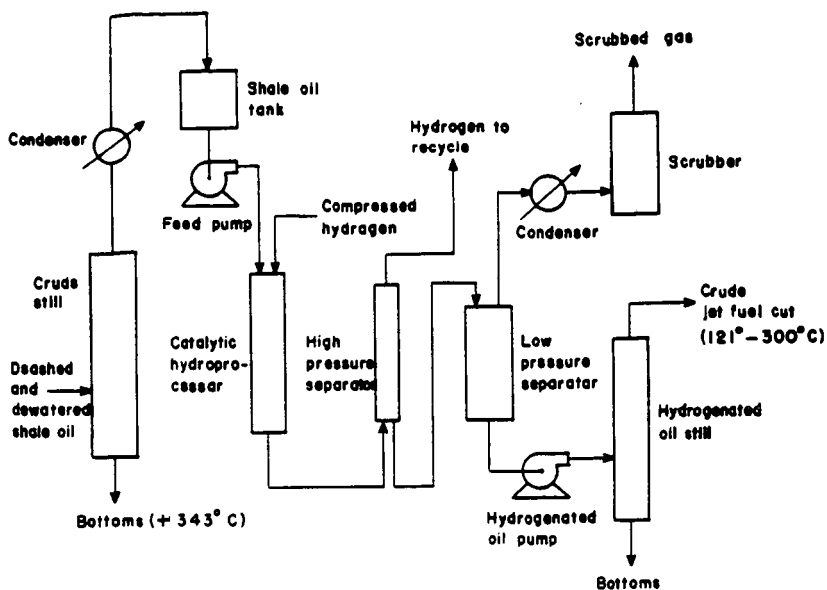


Figure 1. Process Flow Diagram to produce Shale Oil Jet Fuel

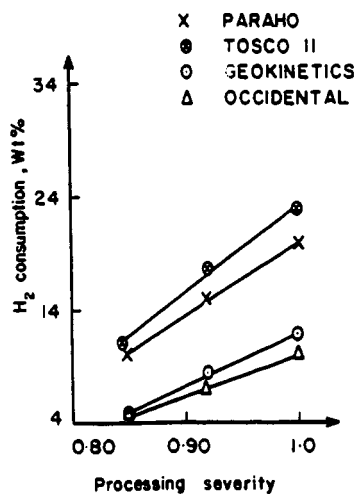


Figure 2. Hydrogen Consumption in Shale Oil Hydroprocessing

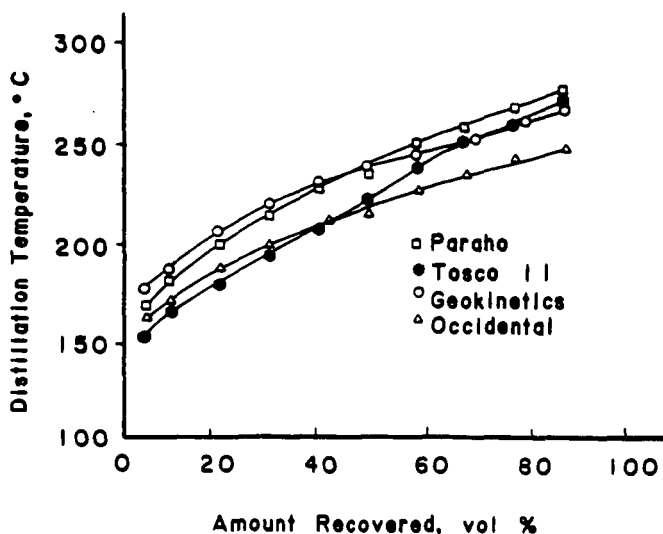


Figure 3. High severity Shale Oil Jet Fuel Distillation

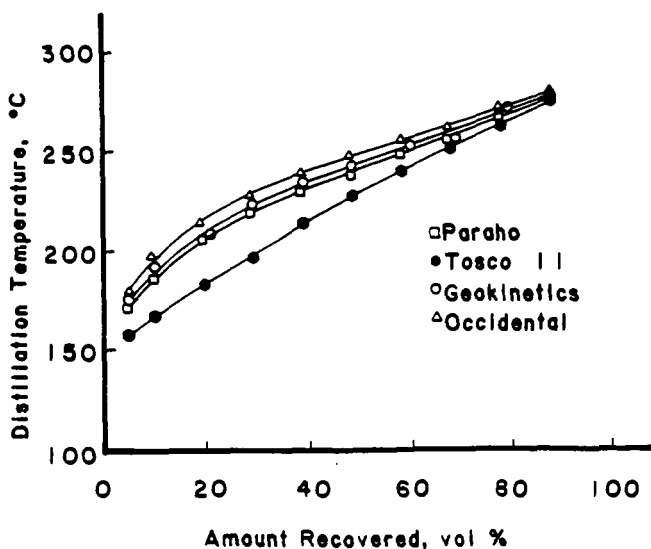


Figure 4. Medium severity Shale Oil Jet Fuel Distillation



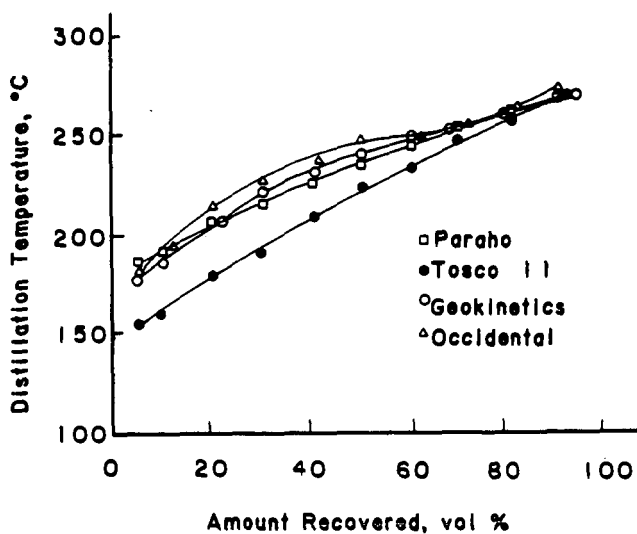


Figure 5. Low severity Shale Oil Jet Fuel Distillation

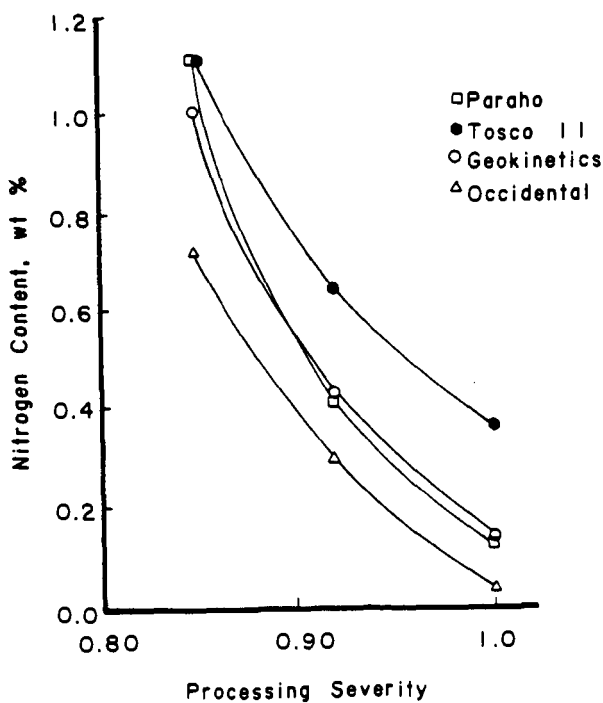


Figure 6. Nitrogen content in Shale Oil Jet Fuel